KFA

KERNFORSCHUNGSANLAGE JÜLICH GmbH

Contributions for the
Sixth London International Conference
on Carbon and Graphite

CARBON 82

Papers to be read at the Conference in
Imperial College, London
20. – 24. September 1982

compiled by

W. Delle

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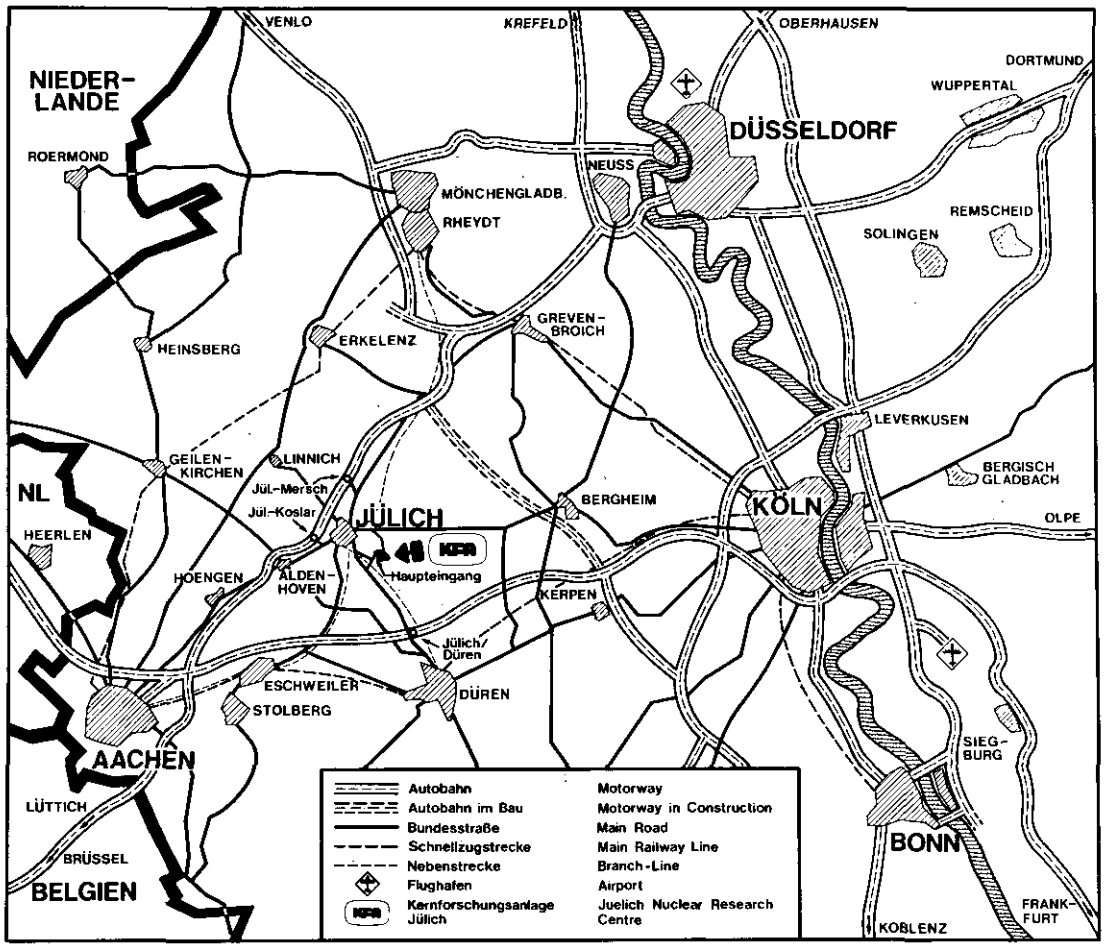

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CONTRIBUTION FOR THE
SIXTH LONDON INTERNATIONAL CONFERENCE

CARBON'82

ON

C A R B O N AND G R A P H I T E

SEPTEMBER 20TH - SEPTEMBER 24TH, 1982

COMPILED BY
W. DELLE

ABSTRACT

This report is the compilation of a number of papers prepared by KFA Jülich GmbH for the Sixth London International Conference on Carbon CARBON'82 which will be held at London in the Imperial College, 20-24 September, 1982. The presentations deal with objectives of manufacture, nuclear application and reactivity of carboneous materials.

The results described were partly achieved in the frame of the Project "Hochtemperaturreaktor-Brennstoffkreislauf" (High Temperature Reactor Fuel Cycle) that includes the partners Gesellschaft für Hochtemperaturreaktor-Technik mbH, Hochtemperatur-Brennelement GmbH, Hochtemperatur-Reaktorbau GmbH, Kernforschungsanlage Jülich GmbH, NUKEM GmbH, Sigri Elektrographit GmbH, Ringsdorff-Werke GmbH and is financed by BMFT (Federal Ministry for Research and Technology) and the State of Nordrhine-Westfalia.

Beiträge zur 6. Internationalen Konferenz in London

CARBON'82

über Kohlenstoff und Graphit vom 20. - 24. September 1982

zusammengestellt von
W. Delle

KURZFASSUNG

Dieser Bericht enthält die Zusammenstellung von Beiträgen der KFA Jülich GmbH für die 6th International Conference on Carbon and Graphite CARbon'82, die in London abgehalten wird. In den Vorträgen werden Fragen der Herstellung, nuklearen Anwendung und der Reaktivität kohlenstoffhaltiger Materialien behandelt.

Die im Bericht beschriebenen Ergebnisse entstanden zum Teil im Rahmen des HTR-Projekts "Hochtemperaturreaktor-Brennstoffkreislauf" mit den Partnern Gesellschaft für Hochtemperaturreaktor-Technik mbH, Hochtemperatur-Brennelement GmbH, Hochtemperatur-Reaktorbau GmbH, Kernforschungsanlage Jülich GmbH, NUKEM GmbH, Sigri Elektrographit GmbH und Ringsdorff Werke GmbH. Es wird vom Bundesministerium für Forschung und Technologie und vom Land Nordrhein-Westfalen gefördert.

CONTRIBUTIONS FOR THE

SIXTH LONDON INTERNATIONAL CONFERENCE ON CARBON AND GRAPHITE

CARBON'82

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C o n t e n t s

1. Einleitung

Die Society of Chemical Industry veranstaltet in der Zeit vom 20. - 24. September 1982 die 6th London International Carbon and Graphite Conference CARBON'82. Diese Tagung fand bisher im Abstand von jeweils 4 Jahren statt, wobei mit dem Arbeitskreis Kohlenstoff der Deutschen Keramischen Gesellschaft alle 2 Jahre gewechselt wurde. Ab 1984 wird sich Frankreich an der Ausrichtung der europäischen internationalen Kohlenstoff-Konferenz beteiligen, und im Jahre 1986 wird sie wieder in Deutschland abgehalten. In den Jahren zwischen den europäischen Tagungen findet im Turnus von 2 Jahren die amerikanische Kohlenstoff-Konferenz statt.

Gegenstand der Diskussionen sind Fragen des natürlichen Vorkommens (Kohlenstoff und Graphit von geologischem Ursprung), der Herstellung von Kunstkohlekörpern (aus gasförmigen, flüssigen und festen Kohlenwasserstoffen), neuer Formen (Kohlenstoffasern, Schäume und glasartige Kohlenstoffe, der Einlagerungs- und zusammengesetzten Verbindungen, der Struktur und des Aufbaus (Kristall- und Porenstruktur, Charakterisierung von Defekten), der Eigenschaften (thermische, elektrische, mechanische sowie chemische Eigenschaften und ihre Messung) und der Anwendungen (industrielle Verwertung sowie Anwendungen in der Chemie, Elektrochemie, Metallurgie, Chemie der Polymere, Luftfahrt, Nuklear- und andere Energieumwandlungsarten sowie Biologie und Medizin).

In der KFA Jülich wird seit vielen Jahren auf dem Gebiet des Kohlenstoffs geforscht, weil er wegen seiner günstigen nuklearen und Hochtemperatureigenschaften an verschiedenen Stellen im gasgekühlten Hochtemperaturreaktor eingesetzt werden kann. So findet er als Reflektor- bzw. Strukturmaterial in Form von Graphit und Kohlestein Verwendung. Graphitische Matrix mit den Rohstoffen Natur- und Petrolkoksgraphit sowie Kunstharzbinder wie auch pyrolytischer Kohlenstoff und Siliziumkarbid als Hüllwerkstoffe für Brennstoffkerne kommen in HTR-Brennelementen in Anwendung.

In den letzten Jahren wurden, aufbauend auf Erfahrungen aus der nuklearen Anwendung, neue kohlenstoffhaltige Materialien entwickelt, die als Gußformen in der Glas- und Metallindustrie besondern gut verwendet werden können. Dieses sog. Coat-Mix-Material kann mit hoher durchgehender Porosität hergestellt werden, was seine Imprägnierung mit flüssigen Medien erlaubt. Ein weiterer Forschungsbereich der KFA auf dem Kohlenstoffgebiet ist die Entwicklung von Siliziumkarbid nach neuen Verfahren und seine Charakterisierung.

Der vorliegende Bericht enthält die Beiträge zur 6th London International Conference on Carbon and Graphite CARBON'82, an deren Ausarbeitung Mitarbeiter der KFA beteiligt waren.

MANUFACTURING AND APPLICATION OF COAT-MIX MATERIALS

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MANUFACTURING

Starting with coat-mix powder materials the manufacturing process of bulk material is essentially the same as already well known in graphite and ceramic industries (see poster 1 at the end of the report).

INDUSTRIAL APPLICATIONS

The essential features of the coat-mix-based carbon bodies are

- continuous porosity
- homogeneity
- isotropy and the wide scope of possible variation of the material data necessary for the optimization of special technical problems.

So far two main fields of application have become evident.

Glassindustries

In glassproduction a coat-mix mould assures high quality glass surfaces without altering the known production techniques. As compared to conventional mould materials in glassindustry it offers additional advantages for the production because steps as, e.g. pasting and others are not required. Fig. 1 shows two examples of machine manufactured glasses and a reproduction of a Dürer motive with cast glass. The latter shows that even smallest details of the mould negative are reproduced in the glass positive. The mould was in this case obtained by direct copying of a positive gypsum model with plastified coat-mix powder material so that even finest details of the gypsum model were reproduced in the mould.

Metallindustries

Experiments so far show that the material is a good moulding material for foundry work rendering high quality surfaces as well as good crystalline structures. The risk of gas inclusions in the cast body is extremly reduced due to the good gas transparency of the material. Fig. 2 shows an example of a cast medal (tin) giving an impression of the high surface quality and high accuracy in the reproduction of smallest details of the mould.

SILICON CARBIDE

Based on the carbon coat-mix technology a SiC material is at present in its final development stage. The essential features of this material are the same as of the carbon coat-mix material as there are porosity, homogeneity, isotropy. In addition to these characteristics this material offers the well know advantages of SiC like high corrosion resistance at high temperatures and hardness. Of essential importance with respect to other known SiC materials is the fact that the coat-mix material can be treated after the coking process prior to the carbidization in a high temperature process mechanically with the same ease as the carbon materials. The final shape and dimensions of such a machined component are not altered during the high temperature treatment. The material thus offers completely new possibilities for an economic production of SiC components in particular of those having complicated structures.

Some possible fields of industrial application are:

- moulding material for metals foundry work
- manufacturing material for ceramic components
- grinding material
- high temperature filters

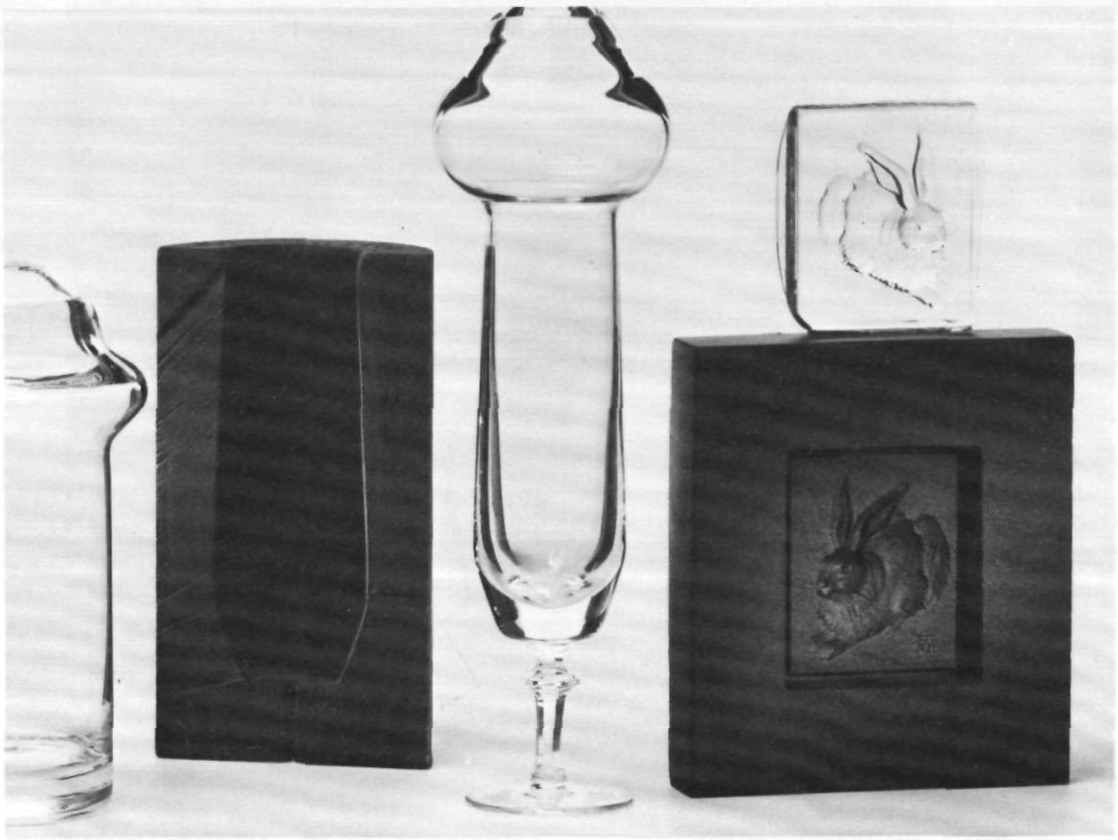

Fig. 1: Coat-mix moulds applied in glass industry

Fig. 2: Coat-mix mould applied in foundry work

THE COAT-MIX PROCESS - A NEW PROCEDURE FOR MIXING CARBON FILLERS AND BINDERS

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In the course of development of the gas-cooled high-temperature reactor, a new mixing procedure for carbon fillers and binders has been developed, the so-called "coat-mix process". Various procedures are known for mixing powders of carbon with binders as a first step in the forming of bodies for the graphite industry[1]. In all these processes, the main goal aimed at, i.e. to form a coating of the filler grains with a homogeneous binder layer, is not fully achieved instead contacts between filler grains without binder bridges and nests of accumulated binder are formed.

PRINCIPLE OF COAT-MIX PROCESS

Following the coat-mix process (Fig. 1) first the binder is dissolved in a suitable solvent and then the filler grains are added to the binder solution to form a slurry. This slurry is injected into a liquid in which the binder is insoluble but the solvent is consolute. During the injection step all the filler grains become completely coated within a fraction of a second with a thin film of binder. After that, a heat treatment converts the slurry to a filterable mass which is subsequently, separated from the liquid and dried. For its technological application and economical advantage, the coat-mix process has been developed with thermoplastic phenolic resins. Fig. 2 shows filler grains of a premium coke before and after mixing according to the coat-mix process.

SOLVENT PROCESS

Alcohol is used as solvent for the binder. The suspension of filler grains in the alcoholic solution is injected into water, the so-called "precipitating liquid", in which the phenolic resin is insoluble but with which the alcohol is miscible.

BASE-ACID PROCESS

For this process a phenol-formaldehyde resin binder is dissolved in an aqueous alkaline medium, e.g. sodium hydroxide, and the slurry is injected into acidified water as the precipitating liquid. In the course of this process first the phenol-formaldehyde resin forms a salt soluble in water. Injection into the acidic precipitating liquid then causes the binder to be deposited on the filler grain surfaces.

SYNTHETIC-BASE-ACID PROCESS

In this case, first the phenol formaldehyde resin binder is synthetized by mixing an aqueous formaldehyde solution with phenol and a catalyst. The resulting aqueous solution containing the resin is then treated in the same manner as previously described.
The advantages of this procedure are that it is not necessary to evaporate the binder solution or te re-dissolve the resin. In addition to saving of time and energy, the binder is more homogeneous and reproducible than the solid resin.

1 Mantell, Ch.L., "Carbon and graphie handbook" Interscience Publishers: New York, 1968, 266

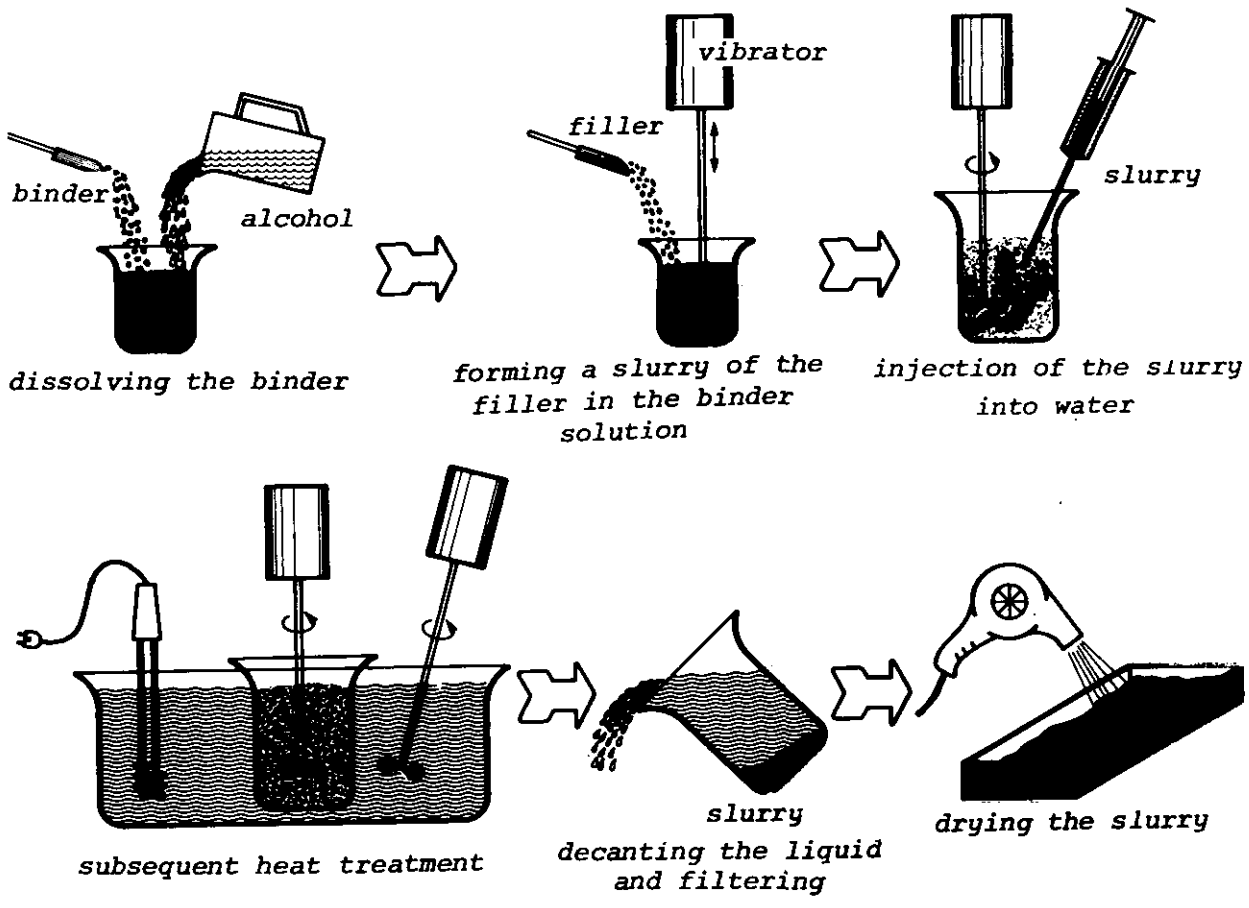

Fig. 1: Diagrammatic view of the coat-mix process

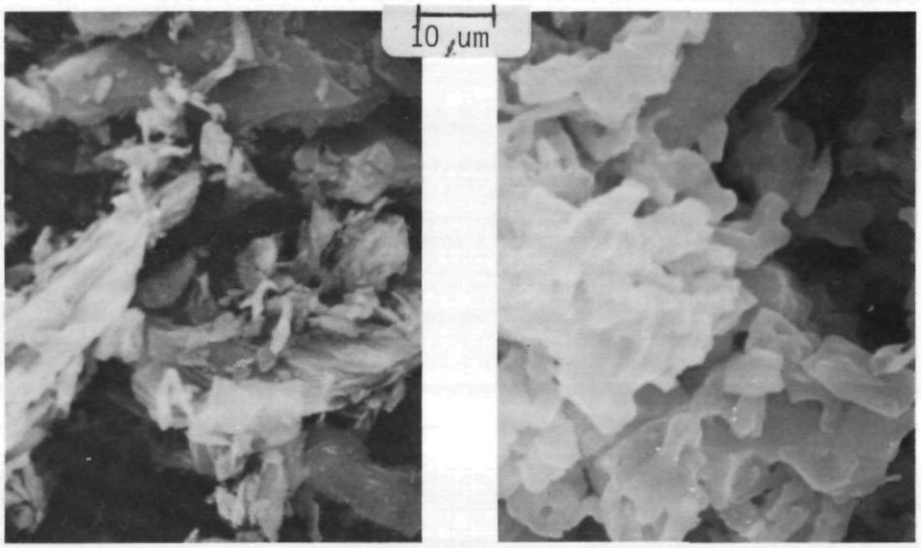

Fig. 2: Filler grains of premium coke, left side before and right side after mixing according to the coat-mix process (SEM pictures)

EXPERIENCES WITH A MODEL FOR IRRADIATION INDUCED CHANGES IN MATERIAL PROPERTIES OF GRAPHITE

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INTRODUCTION

The semi-empirical model for irradiation induced changes in the material properties of graphite was presented at an earlier conference[1]. Subsequently, it has been further developed and applied to describe experimental data for extrapolation and interpolation purposes. Temperature change effects[2] and irradiation induced creep[3] have also been studied[4]. All the recent work is available in the form of a company report[4], a short review of which is given by this paper.

THEORETICAL

The model was derived using the concept of equivalent temperatures[5, 6]. Beyond this concept, having merely the properties of a transformation formula an explicit expression for the irradiation damage was established. The damage formula can be applied to any of the properties: dimensions, Young's modulus, thermal conductivity and coefficient of thermal expansion. In each case the damage is a function of the two independent variables, irradiation temperature and irradiation dose. They are truly independent variables since with increasing dose the thermal history effects are accounted for.

The model works on the premise that the specific kinds of damage listed above are caused by the simultaneous action of three changes in the basic properties of the crystallites. They are the c-axis expansion, the contraction in the direction perpendicular to the c-axis, and the so-called early damage which is caused by small groups of interstitials at an early stage of the irradiation. According to this premise a functional description of each of the three crystalline property changes is obtained which are superposed with appropriate coefficients (importance factors) to describe the damage in its various kinds. The phenomenon of crack closure is considered as only initially affecting the coefficients.

APPLICATION

The model contains a number of unknown parameters such as activation energies, rate of c-axis expansion etc., some being parameters without physical meaning which are introduced for no other reason than to improve the data fitting. Most of the parameters serve the purpose of describing the crystalline changes and are therefore common to all graphite grades. Apart from these global parameters there are also the coefficients employed for superposition of the crystalline changes. They are specific for each graphite and reflect the relative importance of the three crystalline processes.

Thus, subtracting the general damage properties exhibited by the crystallites, there are at the most three unknown parameters with respect to one selected graphite grade and one specific property change in a specified direction. This disclosure is important for application purposes such as extrapolation and interpolation of experimental data points. The model provides the extrapolation features of either a parabola or in some cases a line

which means that ideally only two or three measured property changes with the corresponding irradiation temperatures and irradiation doses suffice for the model to provide the graphite property changes for a large range of temperatures and doses. In practice, because of functional interdependency and the presence of statistical errors in the measurements, it is advisable not to rely on only three data points. Instead one isothermal irradiation experiment clearly showing the influence of the expanding graphite crystallites is preferred.

As an example of such an extrapolation exercise, Fig. 1 shows data points obtained at temperatures near to 400 °C. In a least squares fit to the data the three unknown coefficients were determined such that irradiation experiments concerning the chosen property can be predicted for all irradiation temperatures up to 1500 °C.

The "global" parameters were determined prior to this by simultaneous least squares fitting of more than 10 000 experimental data points comprising all available information in a data bank containing at least 10 years of irradiation experience in graphite property changes. The only restriction in the use of this data was the selection of graphite grades with experimental data showing expansion with respect to the dimensional changes and one fully described curve with respect to the other property changes.

The model opened up the possibility of cataloguing all property changes of all graphite grades with sufficient experimental support. The task was achieved by listing the coefficients of relative importance. A statistical error was also provided. It was derived from the mean square deviation redistributed according to the law of error propagation in order to estimate the uncertainty of the important factors.

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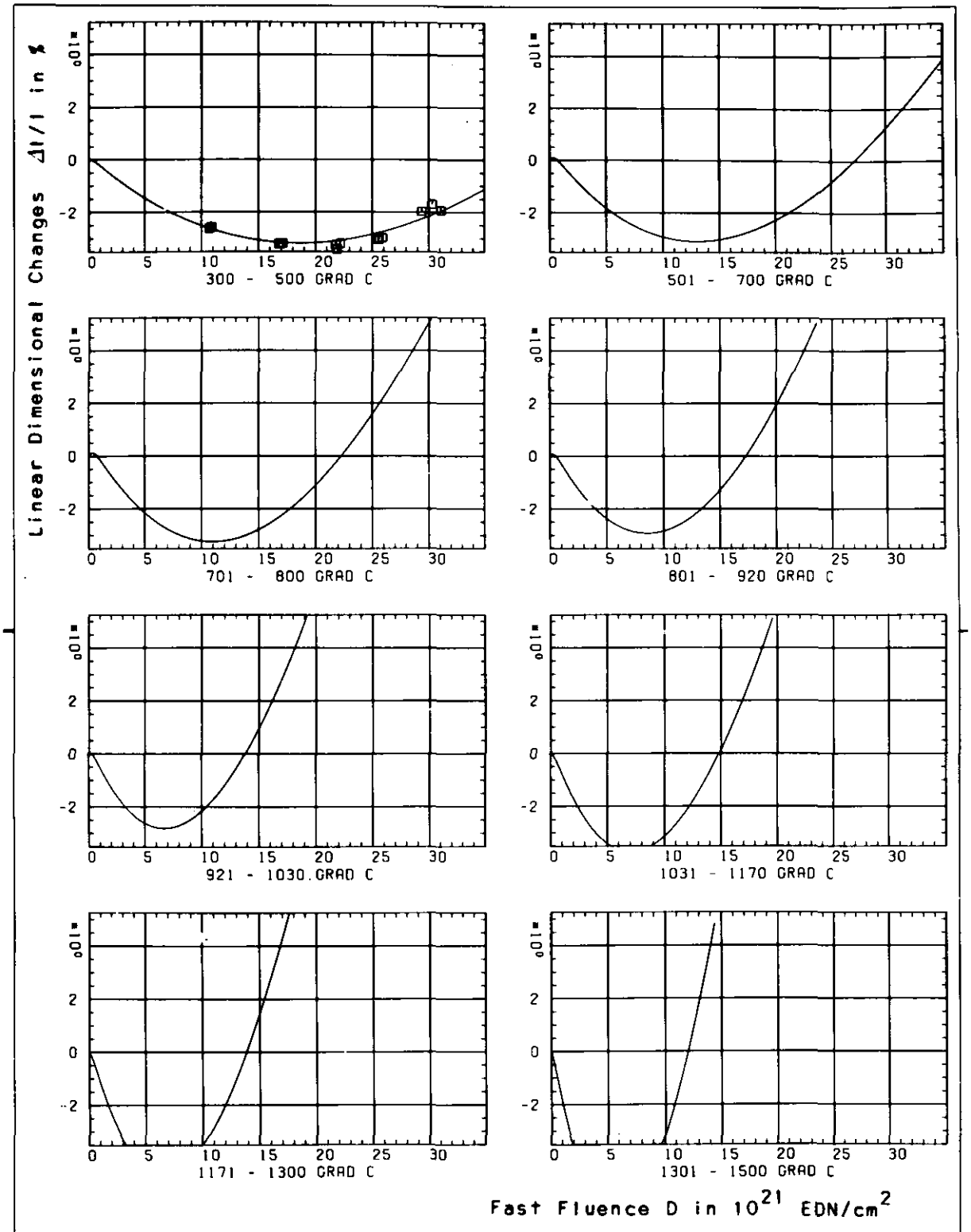

Fig.1: Linear Dimensional Changes as a Function of Temperature and Fast Fluence - Axial Direction

IRRADIATION CREEP PERFORMANCE OF GRAPHITE UP TO HIGH NEUTRON FLUENCE

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INTRODUCTION

For the safe design of the pebble bed High Temperature Reactor (HTR) irradiated property data for the reflector graphite are needed. Irradiation creep data at the relevant temperatures are essential in this respect. Accelerated creep tests at 300 and 500°C are under way in the HFR Petten in high flux positions since 1977 [1,2].

According to some publications in recent years [3,4,5] creep tests performed in a lower fast neutron flux should lead to an enhanced secondary creep rate or creep coefficient. As a check on this, an additional series of analogous creep tests with the same graphite, at the same temperatures, but at a flux level up to four times lower is being carried out.

Typical unirradiated properties of the investigated graphite are summarised in table 1. All specimens were taken in the direction parallel to the extrusion axis.

Apparent density / gcm^{-3}		1.74
Young's modulus / GPa (sonic measurement)	∥	8.55
	⊥	7.40
Tensile strength / MPa	∥	10.80
	⊥	9.05
CTE (20-500°C) / $10^{-6}K$	∥	4.40
	⊥	4.95
Anisotropy factor (CTE)		1.12

Table 1: Typical properties of ATR-2E graphite

RESULTS

Figs. 1a-c show the dimensional change measurement points. The data are corrected for irradiation induced changes of Young's modulus and CTE including creep strain effects. The solid lines are polynominal least quare fits according to the expressions quoted in fig. 1. The secondary creep strain ε_c and the derivative of creep strain with respect to fluence, normalized to unit stress, i.e. the secondary creep coefficient K are plotted versus fluence in figs. 2a-c. Figs. 3a,b compare the fluence curves of Young's modulus and of the secondary creep coefficient, both normalized to their corresponding values at the fluence of 1 x 10^{21} cm^{-2} (EDN). Both curves were hoped to coincide thus advising a method to extrapolate high fluence creep behaviour from low fluence data by means of available Young's modulus change data [6]. In fig. 4 comparison is made between creep strain measurement points from the high and the low flux creep experiments. The points at about 0,4 x 10^{21} cm^{-2} (EDN) are assumend to represent the maxi-

mum primary creep strains under low and high flux conditions respectively. In the low flux situation they are considerably larger than the unirradiated elastic strain. The secondary creep strain rates up to 2,0 x 10^{21} cm^{-2} (EDN) tend to be nearly equal for low and high neutron flux at both temperatures, with some deviation arising from three measurement points at 300°C in the high flux condition.

DISCUSSION

A general feature of these investigations is a steadily decreasing secondary creep rate with fluence. The trend apparently becomes reversed somewhere beyond 1 x 10^{22} cm^{-2} (EDN). This is in qualitative agreement with the creep model proposed by Kelly et al. [6,7] which implies that irradiation induced structural changes directly affect the macroscopic creep strain. The structural changes are quantified by changes of the structural component of Young's modulus as expressed by the structural factor S (x) in figs. 3a,b. Here the quantitative agreement between the curves of S (x) and the normalized creep coefficient is not good. An extrapolation of low fluence to high fluence creep rates by means of S (x) would furnish a too optimistic creep behaviour.
The transverse compressive creep strains exhibit considerable scatter which was even larger in the tensile mode. However, a rough estimate of Poisson's ratio in creep was made to be ν_c = 0,4 maximum in the shrinkage region and tending to zero after shrinkage reversal.
Experimental evidence so far is that the fast flux only affects the primary creep. This might lead to the conclusion that whenever a flux effect on the secondary creep coefficient was claimed [3,4,5] this was perhaps due to an incorrect assumption on the amount of primary creep strain. In instances when explicit measurement of primary creep strain was not available, it was assumed that the maximum primary creep strain was equal to the elastic strain, e.g. in restrained shrinkage experiments [4] and in the matrix creep experiment in the DRAGON Reactor [3].

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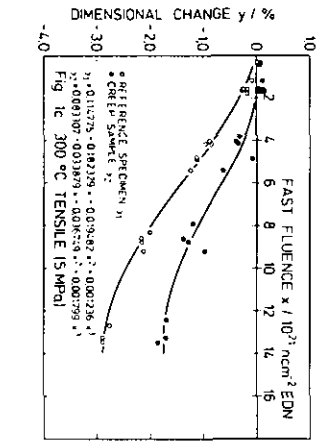

Fig. 1 a–c: Dimensional changes of ATR-2E at 300°C and 500°C

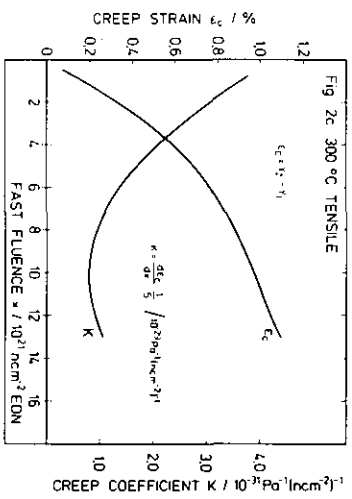

Fig. 2 a–c: Creep strain and creep coefficients of ATR-2E at 500°C (tensile and compressive) and 300°C (tensile)

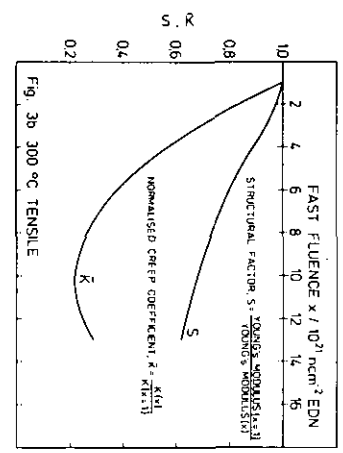

Fig. 3 a–b: Comparison of structural factor with normalised creep coefficients

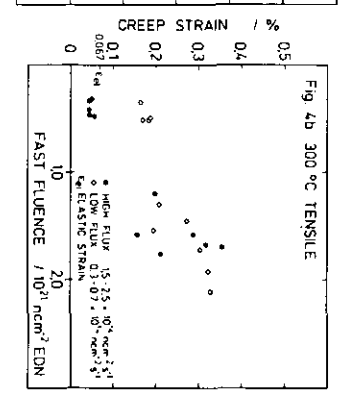

Fig. 4 a–b: Comparison of high and low flux level creep strains for ATR-2E at 300°C and 500°C

EFFECT OF ANNEALING ON IRRADIATION INDUCED CHANGES IN GRAPHITE AND FUEL MATRIX

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EXPERIMENTAL

Graphite and fuel element matrix specimens investigated were irradiated in the High Flux Reactor Petten/The Netherlands. The fast neutron fluences accumulated were in the range 1.2 10^{21} cm^{-2} to 5.2 10^{21} cm^{-2} EDN, the irradiation temperatures between 420°C and 1450°C. The irradiation induced changes measured were linear dimensions, electrical resistivity, Young's modulus and thermal conductivity. Some of the specimens were heat-treated at temperatures from about 100 degree higher than the irradiation temperature up to 2000°C for between 4 and 60 hours. The different temperature levels were held for different time intervals. Details concerning the heat-treatment history can be taken from figures 1 and 2. The furnace was at first evacuated to about 10^{-5} bar and after 16 hours of degassing argon was introduced at a pressure of about 750 mb at 2000°C. The thermal conductivity samples were annealed in a vacuum resistance furnace. At the maximum temperature of about 1500°C a pressure of about 10^{-5} bar was achieved. In a combined equipment, both thermal conductivity and electrical resistivity were measured between 100°C and 1000°C. (1)

RESULTS

Linear Dimensions

Dimensional recovery on annealing occurs only in specimens which have accumulated small fluences. The annealing out of the irradiation induced growth of samples becomes more and more difficult at higher fluences and irradiation temperatures. In the experiments reported here, no dimensional changes by annealing could be observed even at annealing temperatures of 2000°C for 24 hours.

Physical Properties

Significant changes in physical properties were only found at annealing temperatures above about 1400°C, and annealing at temperatures of 1700°C and higher produced a decrease in electrical resistivity and Young's modulus (fig. 1 and 2). The Young's modulus of the fuel element matrix which as the final production step was heat-treated at 1800°C decreased by the annealing at 2000°C even below the pre-irradiaton value. High temperature thermal conductivity of a specimen irradiated at 420°C started to increase at 800°C in a very small amount. Somewhat more occurred at 1050°C.

A more pronounced improvement in thermal conductivity was found after the heat-treatment at 1250°C and a drastic increase at 1450°C (fig. 3). High temperature electrical resistivity measured on the same sample was changed a little after annealing at 1050°C. At higher heat-treatment temperatures a significant decrease of electrical resistivity was observed.

DISCUSSION

During irradiation at low temperatures, single vacancies are mainly produced. Between 300°C and 600°C the damage consists of interstitial groups and of randomly distributed vacancies. The effect of annealing is to decrease the number and to increase the size of interstitial groups. Single vacancies may be annealed out by recombination. (2) At still higher irradiation temperatures the tendency for the formation of large interstitial loops as well as large vacancy loops increases. It is assumed that the annealing out at temperatures above irradiation temperature affects more the number and size of the defects than the number of carbon atoms. This may be the reason why although the conductivities increased the linear dimensions were not changed by the heat-treatment. The change in Young's modulus seems to be due to the annealing out of stresses in the intercrystalline regime and the binder phase.

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ACKNOWLEDGMENT

The results described were obtained in the framework of the HTR Project "Hochtemperatur- Brennstoffkreislauf" (High Temperature Reactor Fuel Cycle), HBK, which includes the partners Gesellschaft für Hochtemperaturreaktor-Technik mbH, Hochtemperaturreaktor-Brennelement GmbH, Hochtemperatur-Reaktorbau GmbH, Kernforschungsanlage Jülich GmbH, NUKEM GmbH and Sigri Elektrographit GmbH/Ringsdorff-Werke GmbH. The project is financed by the Federal Ministry for Research and Technology and by the State of North Rhine-Westphalia.

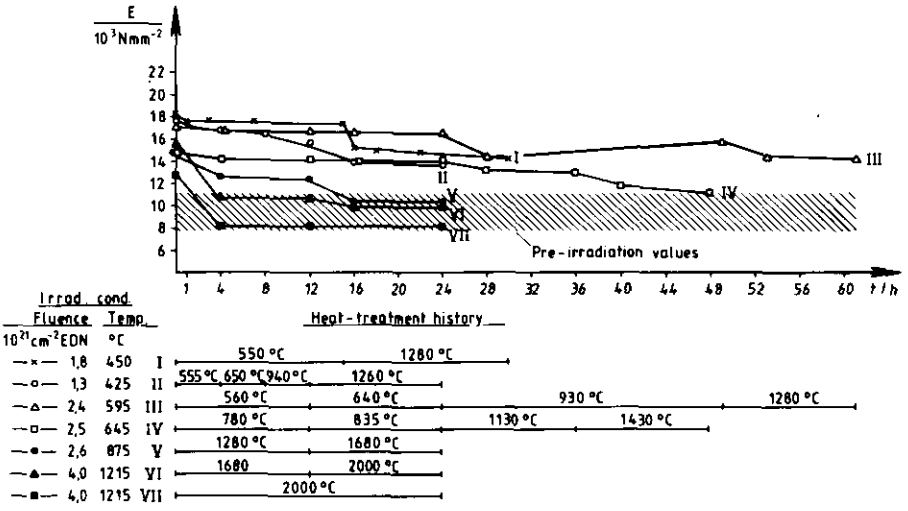

Fig. 1: Annealing of irradiation induced changes in Young's modulus of the pitch coke graphite ASR-2E

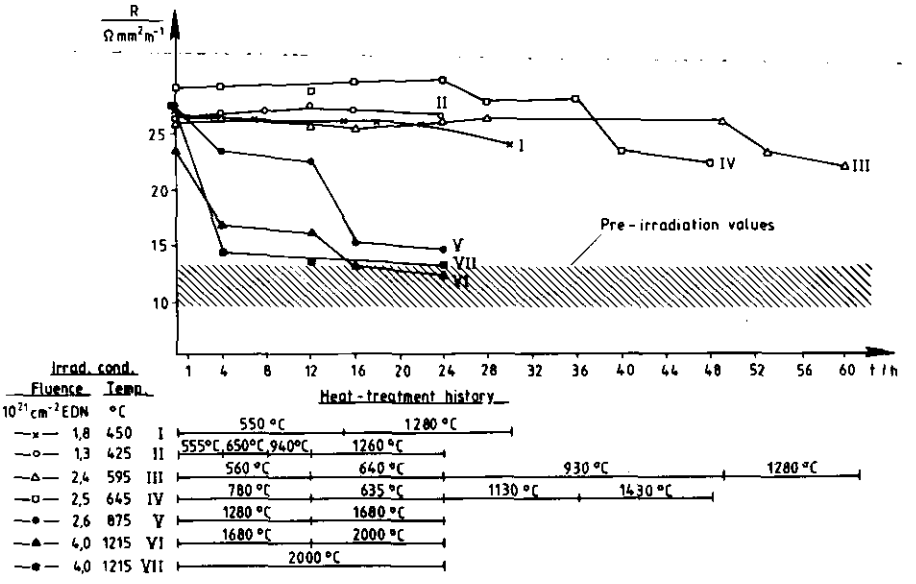

Fig. 2: Annealing of irradiation induced changes in electrical resistivity of the pitch coke graphite ASR-2E

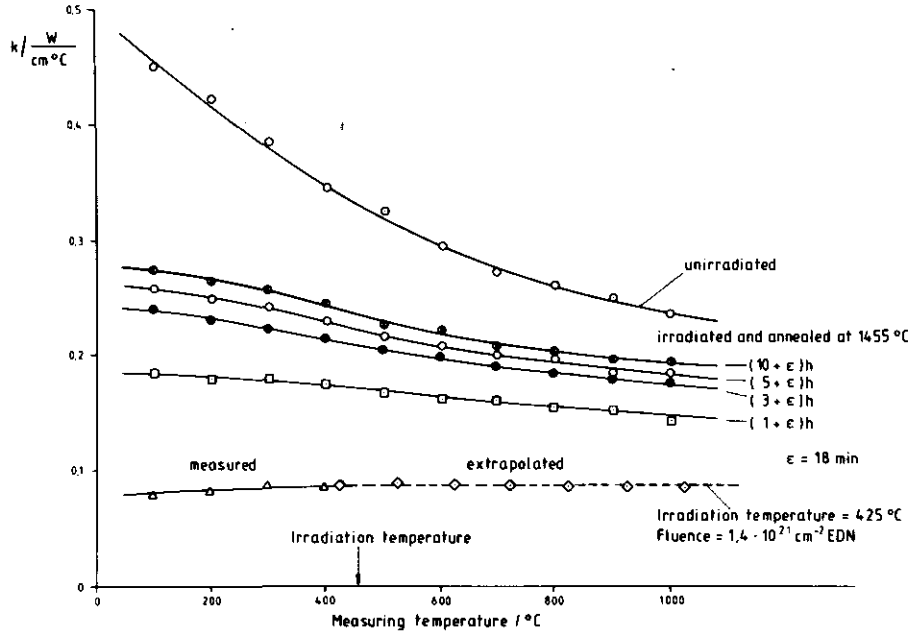

Fig. 3: Annealing of thermal conductivity of the graphitic fuel matrix A3-27

EFFECT OF FAST NEUTRON IRRADIATION AND CORROSION ON PHYSICAL PROPERTIES ON NUCLEAR GRAPHITE AND FUEL MATRIX

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Graphite and matrix materials in the core of the High Temperature Gas-Cooled Reactor (HTR) are subject to fast neutron irradiation damage. Furthermore small concentrations of moisture present as an impurity in the helium coolant as well as O_2 and CO_2 lead to corrosion effects the mechanisms being mainly temperature dependent. The graphite properties which make this material very favourable to the application in nuclear reactors are significantly modified by irradiation and corrosion. The question arises whether these changes have a detrimental or a beneficial effect on the material behaviour. There is also the possibility that a deterioration of one of the properties may be offset by an improvement in another.

The key property is porosity. The t o t a l p o r o s i t y of graphite and fuel element matrix is decreased by irradiation, because the crystallites expand into the micropores and the macropores serve as a buffer volume for the dimensional changes within the bulk material. The reduction in porosity depends on the degree of graphitization. In well graphitized materials with large crystallites, the reduction is smaller than in poorly graphitized materials. A minimum porosity is reached when the turn-around of dimensional changes is passed with increasing fluence. The built up stresses increase and may lead to the formation of new pores (fig. 1). In nuclear graphites, o p e n p o r o s i t y is also reduced by fast neutron irradiation. In contrast, the investigations of fuel element matrix materials with various filler compositions and resin binder as well as final heat-treatment temperature of 1800°C showed that the open porosity of this group of materials is increased by fast neutron exposure (fig. 2). This increase is caused by the irradiation induced formation of large open pores possibly due to the opening of originally closed pores. After a certain fluence depending upon material composition and irradiation temperature, open porosity decreases again to below the pre-irradiation value (fig. 2). The irradiation induced decrease of open porosity is accompanied by a decrease of BET surface, but in the case of matrix material the increase in open porosity at the beginning of the irradiation is associated with an increase of BET surface.

The effect of corrosion on graphite materials in HTR depends mainly upon the temperature. Up to about 850°C the reaction rate is that of the chemical reaction, i.e., the reaction of the reactant in the pores of the materials is the same as that of the gaseous environment. Uniform corrosion all over the accessible graphite block volume occurs with an increase of open porosity and BET surface. This increase is more pronounced in matrix materials than in graphite. At very high burn-off the BET surface decreases again. With increasing temperature, the reaction rate is governed by diffusion of the reactant through the pores of the graphite. A concentration gradient is established and at equilibrium the rate of reactant depletion is balanced by the rate of diffusion through the pores. At very high temperatures, that is higher than 1000°C for the O_2-corrosion and higher than about 1250°C for the water-graphite reaction, the reaction rate is limited by the rate of diffusion of reactant across the gaseous boundary layer. Only the surface of the graphite artefact is attacked.

In an HTR, irradiation and corrosion effects occur simultaneously. In graphite, irradiation causes a reduction in porosity whilst corrosion increases porosity. Under normal service conditions, the porosity will be slightly decreased until the turn-around of the dimensional changes, whereas for fuel element matrix an net increase of porosity can be expected. The mechanical properties are more affected by intercrystalline effects, such as pinning than by porosity changes. This means that under normal operation conditions, Young's modulus and strength are significantly decreased due to the superimposed effects of stress generated new porosity and carbon burn-off. Thermal conductivity is more affected by defects in the lattice than by changes in porosity. Corrosion causes carbon burn-off especially in the binder coke regime. Therefore the restraint of this component against the filler grain thermal expansion (2) is decreased and the C.T.E. increases. When at higher burn-offs the porosity increases marketly the C.T.E. decreases. As a net result from irradiation and corrosion the C.T.E. increases at the beginning of the operation and decreases with time due to both fast neutron irradiation and corrosion.

The simultaneous effects of both irradiation and corrosion as well as the resulting particular property changes are shown in fig. 6.

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ACKNOWLEDGEMENTS

This work has been carried out in the framework of the Project "Hochtemperaturreaktor-Brennstoffkreislauf" (High Temperature Reactor Fuel Cycle) that includes the partners Gesellschaft für Hochtemperaturreaktor-Technik mbH, Hochtemperatur-Brennelement GmbH, Hochtemperatur-Reaktorbau GmbH, Kernforschungsanlage Jülich GmbH, NUKEM GmbH, Sigri Elektrographit GmbH, Ringsdorff-Werke GmbH and is financed by BMFT (Federal Ministry for Research and Technology) and the State of North Rhine-Westphalia.

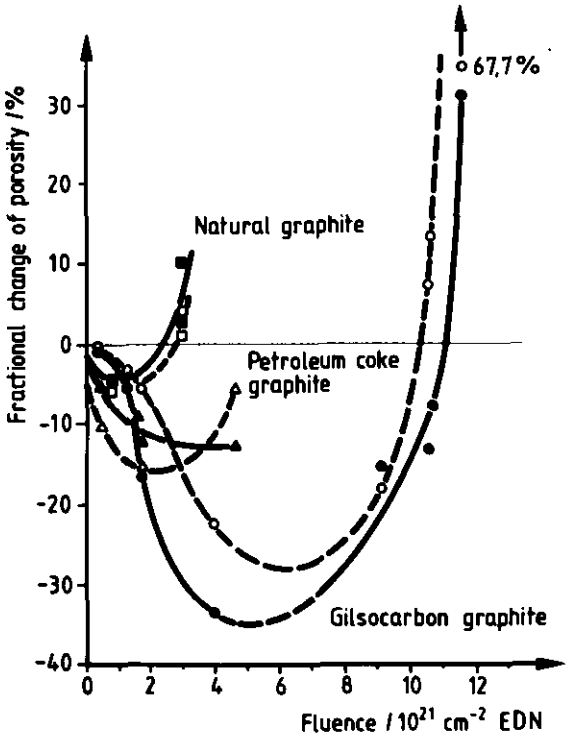
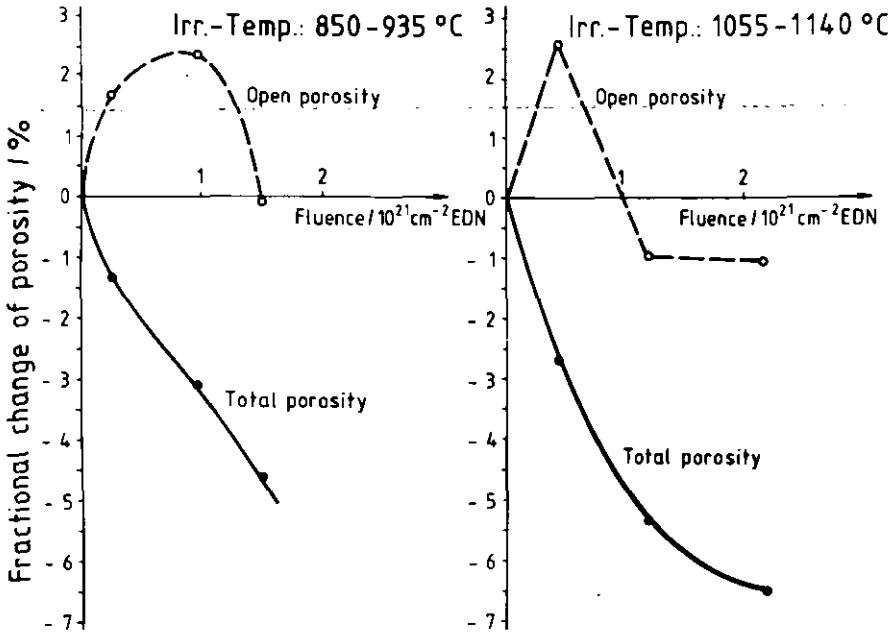


Fig. 1: Changes in total and open porosity of various graphites (1)



Composition: 80 w-% Natural graphite
20 w-% Petroleum coke graphite
Resin binder, final heat treatment temperature 1800 °C

Fig. 2: Changes of open and total porosity of fuel element matrix consisting of 72 W-% natural graphite, 18 W-% petroleum coke graphite and 10 W-% resin binder coke, heat-treatment temperature = 1800° C (1)

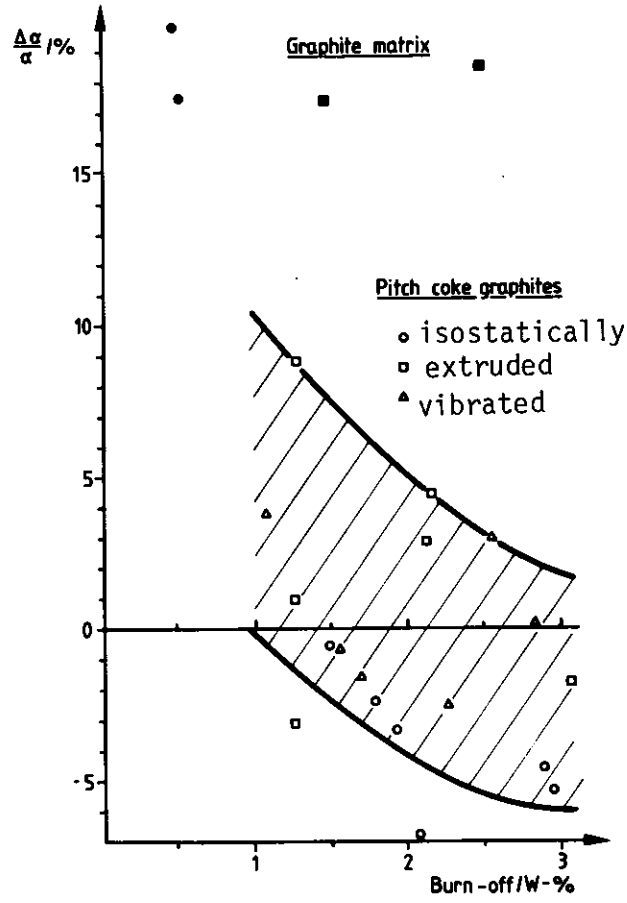


Fig. 3: Correlation between carbon burn-off and fractional change of linear thermal expansion (C.T.E.)

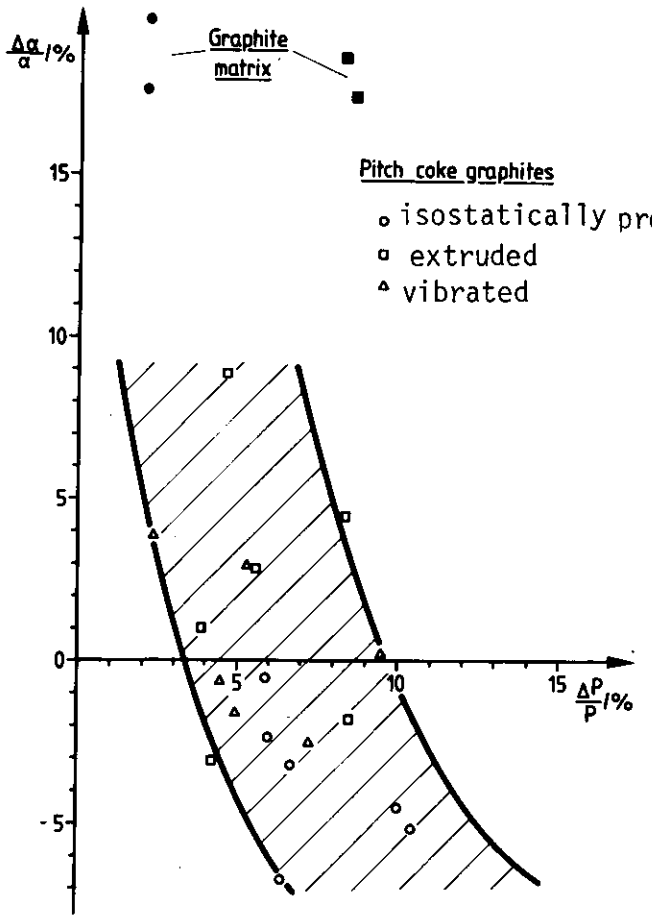


Fig. 4: Correlation between O_2-corrosion induced change of total porosity and linear thermal expansion (C.T.E.)

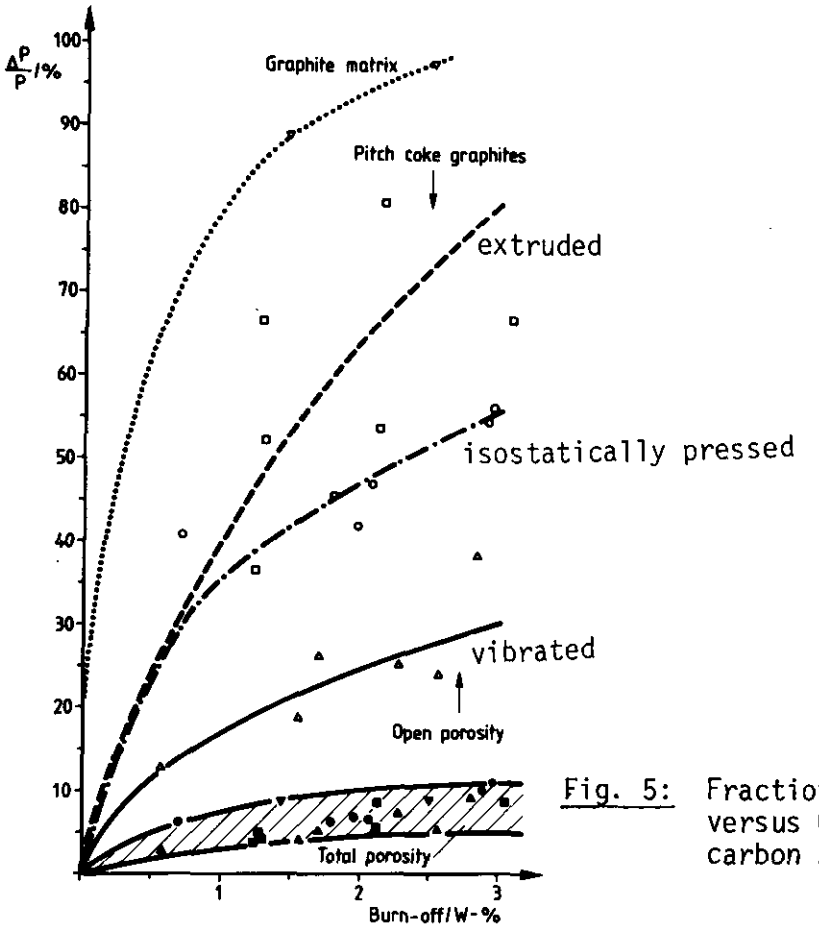


Fig. 5: Fractional change of porosity versus O_2-corrosion induced carbon burn-off

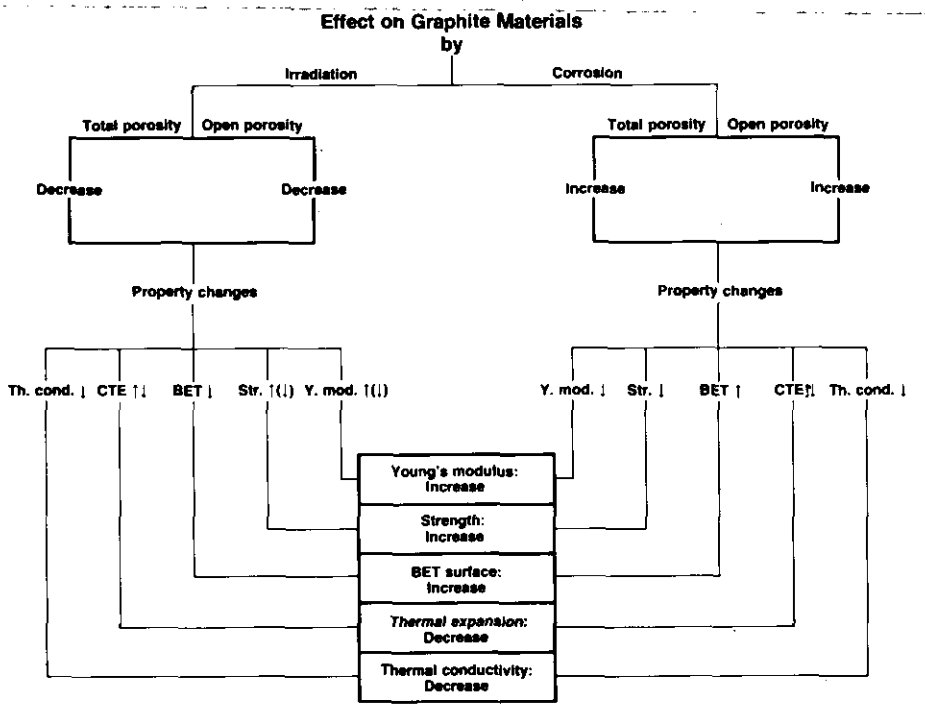


Fig. 6: Effect of fast neutron irradiation and corrosion on some properties of graphite materials
↑ = increase ↓ = decrease

OPTIMIZED GRAPHITIC MATRIX MATERIALS FOR SPHERICAL HTR FUEL ELEMENTS

Schulze, R.-E.[1)], Schulze, H.A.[1)], Rind, W.[2)], Delle, W.[1)]

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2) Firma HOBEG, P.B. 110029, D-6450 Hanau, Fed. Rep. Germany

A comprehensive programme has been carried out for the development and irradiation testing of graphitic matrix materials for spherical HTR fuel elements. The development was performed by NUKEM/HOBEG, Hanau, while irradiation took place in the High Flux Reactor (HFR) Petten, The Netherlands, as part of the joint DRAGON-KFA-EURATOM-RCN/ECN Programme*.

The most significant results of this materials programme are as follows:

1. The development and irradiation testing [1] of graphitic matrix materials have furnished the standard matrix A3-3 which is suitable as a structural material for HTR fuel elements. It is being used for the elements of the AVR and the THTR reactors and has been proved successfully in AVR reactor operation.

2. The development of variants of the standard matrix with the objectives:
   - enlargement of the raw material base
   - simplification of fabrication
   - improvement of product properties
   and the irradiation testing [1] of 18 of these variants have furnished the matrix with synthesized resin A3-27. This variant is also suited for use as a structural material for fuel elements. Elements fabricated with this material are already being tested in AVR reactor operation. Three further variants of the standard matrix (A3-6, A3-5, and A5-2) may be considered as a potential for technological use.

3. Influences by raw material, fabrication and irradiation parameters on material properties and their changes under irradiation could be determined [2] . Their knowledge enables a good understanding of the material behaviour.

The development of matrix materials by NUKEM/HOBEG was performed in two phases (fig. 1). The result of the material optimization of phase I was the standard matrix A3-3 with the raw material composition 64 wt.% natural graphite, 16 wt.% petroleum coke graphite, 20 wt.% phenolic resin binder. In phase II a broad selection of variants of the standard matrix was developed. The targets of development as well as the parameters varied are shown in fig. 1. As the most important result of this second phase the matrix with synthesized resin A3-27 can be regarded. It does not only permit simplified fabrication, but also exhibits improved strength and corrosion properties compared to the standard matrix.

In fig. 2, besides the matrix A3-27 those materials are compiled, which have emerged as most favourable variants from an enlargement of raw material base (A3-6) and improvement of product properties, especially strength (A3-5 and A5-2). Also these variants exhibit improved strength and corrosion properties as well as sufficiently good dimensional behaviour under irradiation.

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*) Partners involved: OECD-DRAGON Project, Dorchester, Dorset, England; Kernforschungsanlage Jülich GmbH, Fed. Rep. Germany; EURATOM; Stichting Reactor Centrum/Stichting Energieonderzoek Centrum, Petten, The Netherlands.

Fig. 3 shows a comparison of the irradiation-induced dimensional change of the fuel matrices A3-3 and A3-27. The differences observed can be attributed to the influences of the three parameters by which the materials differ from each other: the type of binder, the binder coke content and the temperature during final heat treatment.

Fig. 4 gives a comparison between the dimensional changes of specimens of the standard matrix A3-3 and those of spherical fuel elements with A3-3 as structural material. The dimensional changes as a function of the irradiation temperature of the matrix and of the surface temperature of fuel elements are plotted for the mean THTR fluence of 2.5×10^{21} cm^{-2} EDN. The comparison shows the relatively good agreement between the results of matrix specimens and those of fuel elements.

The results described were obtained within the framework of the HTR project "Hochtemperaturreaktor-Brennstoffkreislauf" (High-Temperature Reactor Fuel Cycle) involving the Gesellschaft für Hochtemperaturreaktor-Technik mbH, Hochtemperaturreaktor-Brennelement GmbH, Hochtemperatur-Reaktorbau GmbH, Kernforschungsanlage Jülich GmbH, NUKEM GmbH and Sigri Elektrographit GmbH/ Ringsdorff-Werke GmbH. The project is sponsored by the "Bundesministerium für Forschung und Technologie" (Federal Ministry for Research and Technology) and by the State of North-Rhine/Westphalia.

[1] Schulze, R.-E., Schulze, H.A., KFA-Report Jül-1702, Febr. 1981
[2] Schulze, R.-E., Schulze, H.A., Delle, W., 5th Intern. Conf. on Carbon and Graphite, London, Sept. 1978, proceed. 904-917

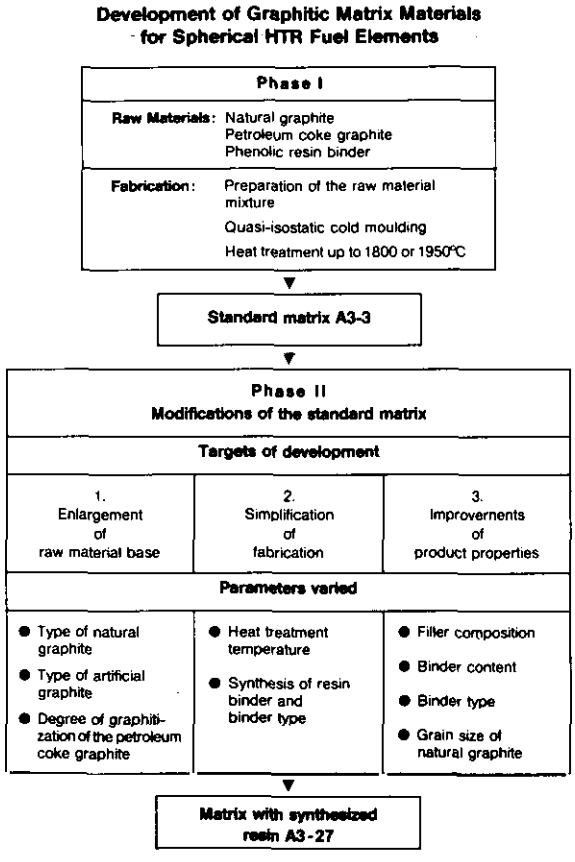

Fig. 1:
Fuel matrices A3-3 and A3-27 as the most important materials resulting from development

Most Favourable Variants for an Enlargement of the Raw Material Base, Simplification of Fabrication and Improvement of Strength Concerning Falling Strength and Corrosion Rate as well as the Irradiation-induced Dimensional Behaviour

Variant	Variation	Falling strength ** related to A3-3	Corrosion rate *** related to A3-3	Dimensional behaviour at THTR operation time dose	Volume shrinkage at 1250°C and THTR operation time dose
A3-6 (enlargement of raw material base)	Other type of natural graphite component	150 %	55 %	mainly isotropic	slightly smaller than A3-3
A3-27 (simplification of fabrication)	Binder synthesis	130 %	60 %	anisotropic * for T > 1000°C	slightly greater than A3-3
A3-5 (improvement of strength)	Elevated content of natural graphite	140 %	60 %	mainly anisotropic * for T > 800°C	smaller than A3-3
A5-2 (improvement of strength)	Smaller grain size of natural graphite and addition of hardener	> 1000 %	not determined	anisotropic * for T > 700°C	corresponding to A3-3

* anisotropic behaviour to a limited extent[1]
** falls of a test sphere from a height of 4 m onto a bed of A3-3 spheres till fracture
*** after 10 h at 1000°C in He of 1 bar with 1 Vol % H_2O

Fig. 2:
The most favourable variants from the modifications of the standard matrix A3-3

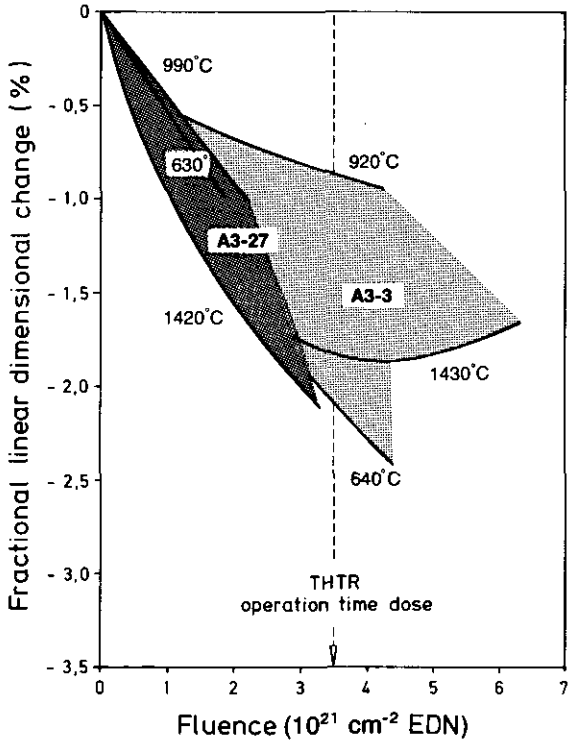

Fig. 3:
Comparison between the irradiation-induced dimensional changes of the fuel matrices A3-3 and A3-27

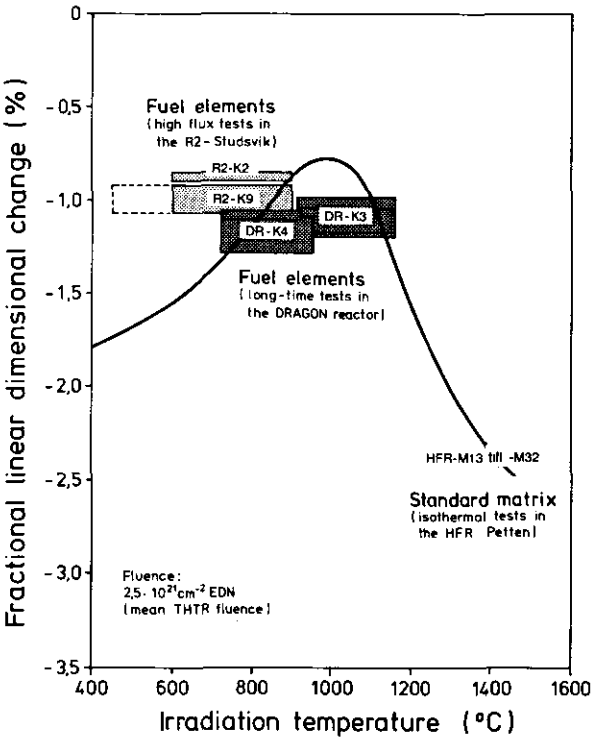

Fig. 4:
Comparison between the dimensional changes of the standard matrix A3-3 and spherical fuel elements, shown for the mean THTR fluence

INVESTIGATIONS OF THE OXIDATION BEHAVIOUR OF FILLERS AND BINDER COKE USING COAT-MIX MATERIALS AS MODEL SUBSTANCES

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Coat-Mix (CM) material is a new carbon based material developed at the Nuclear Research Centre Jülich. At present it is used for the manufacturing of moulds in different industrial branches, e.g. glass and metal industries.
It is therefore of essential importance to know corrosion characteristics at higher temperatures in air. Because of its unique structure it is a good model substance that permits a separate observation of the oxidation behaviour of filler grains and binder coke. For the investigations two different filler materials were used (petroleum coke and graphite).

CM MATERIAL

The CM materials examined in this study were produced in the following way:

- 70 mass % powdered petroleum coke or graphite as filler material were coated according to the CM process with 30 mass % phenol-formaldehyde resin as binder.
- The powder was moulded at 400 K with a pressure of about 0,6 MPa.
- During the following coking step up to 1070 K in an argon atmosphere the binder was completely carbonized, the weight of the remaining binder coke being 17 mass %.
- The bulk was calcined at 1770 K under vacuum.

The most important features of the new materials are:

- a continuous porosity, in this case of about 30 %,
- a complete coating of each filler particle by binder coke.

EXPERIMENTS

Samples were attached to a platinum wire and introduced into a heatable quartz reactor of an electro balance (Cahn RH) permitting the continuous registration of weight changes during experiments until the point of disintegration of the samples.
The specimens were carefully degassed under vacuum and then heated up to the reaction temperature.

Subsequently the samples were cooled down and the oxidizing gas (1/5 O_2 + 4/5 N_2) was introduced at a constant flow rate and definite pressure. Finally the preheated furnace was re-positioned. Further experimental parameters are listed in Tab. 1.

sample dimension	Ø 8 mm, height 16 mm
mass	~1 g
reaction temperature	781 ± 1 K
gas pressure	50 ± 0.5 kPa
flowrate	5 l/h STP

Tab. 1: Experimental parameters

RESULTS AND DISCUSSION

Results are given in Fig. 1 to Fig. 3. The different course of the two curves (Fig. 1) is due to the different reaction rates of the two filler materials (coke and graphite), since the reaction rate of the binder coke is proved to be nearly the same in both cases. It was surprizing that the disintegration of the coke filler samples took only place at a burn off of about 85 % without change of its initial dimensions. Fig. 2 shows scanning electron micrographs of coke filler material before and after oxidation. The right picture indicates clearly that oxidation of the filler takes place via initially burned holes into the binder coke coating. The plot (Fig. 3) reveals that compression strength decreases substantially above a burn off of about 18 %.

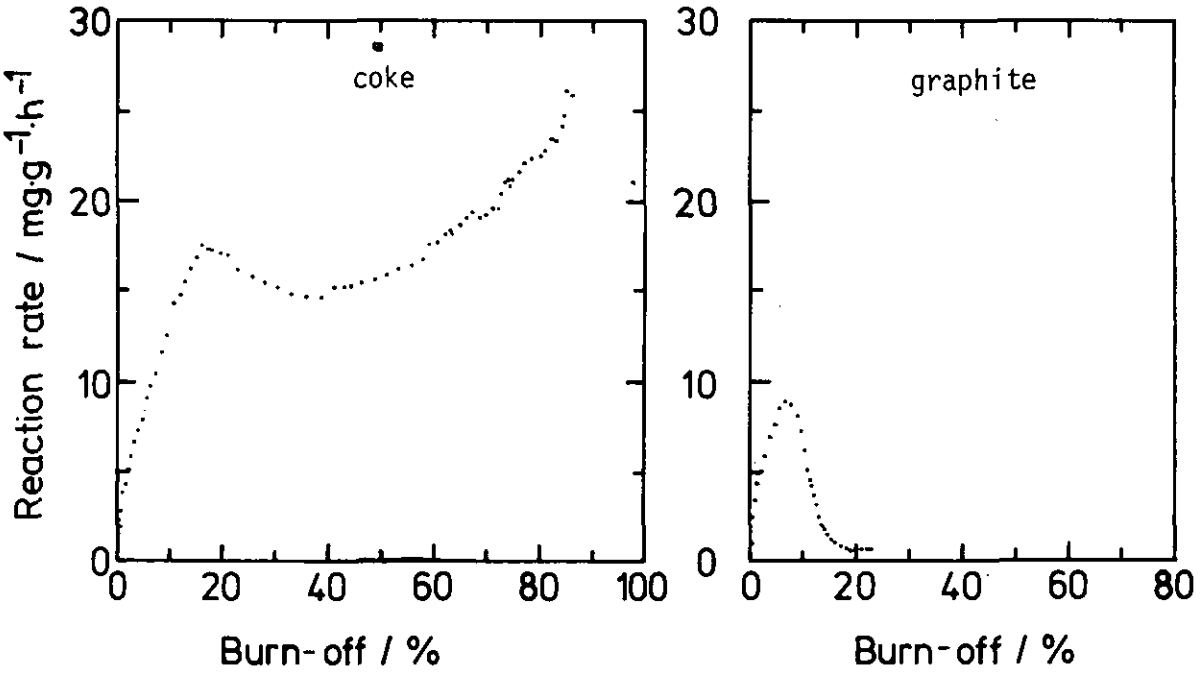

Fig. 1: Experimental plots of reaction rate vs. burn off

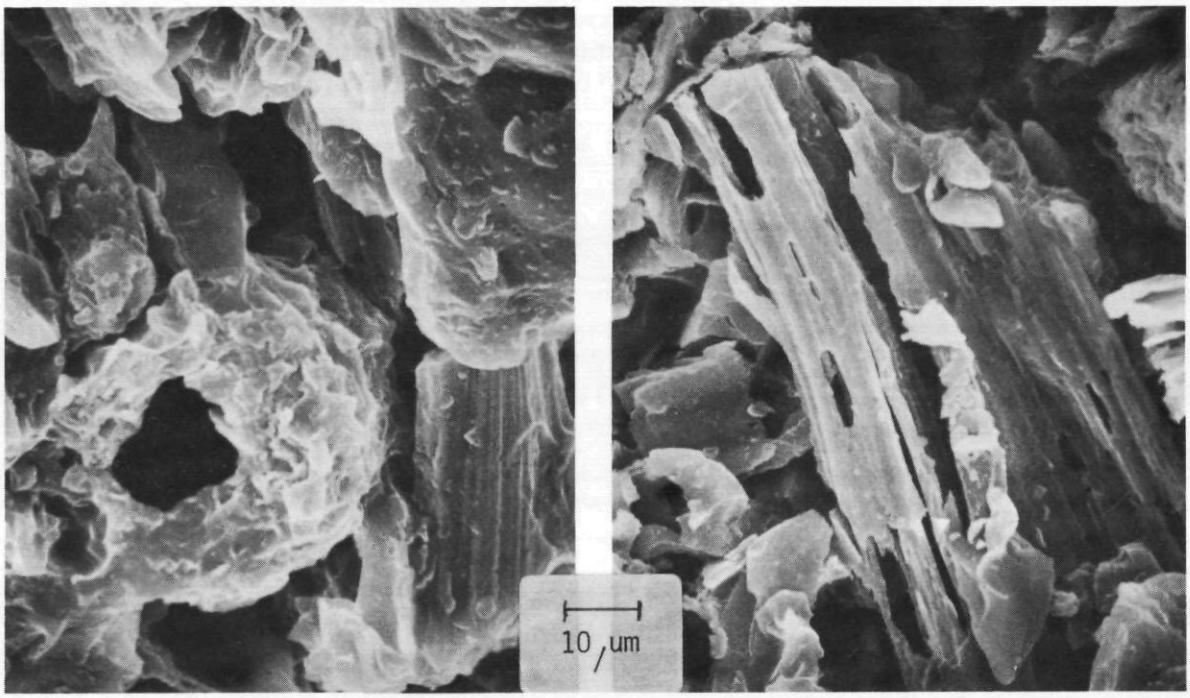

Fig. 2: Scanning electron micrographs of samples with coke filler left side before oxidation, right side after 51 % burn off

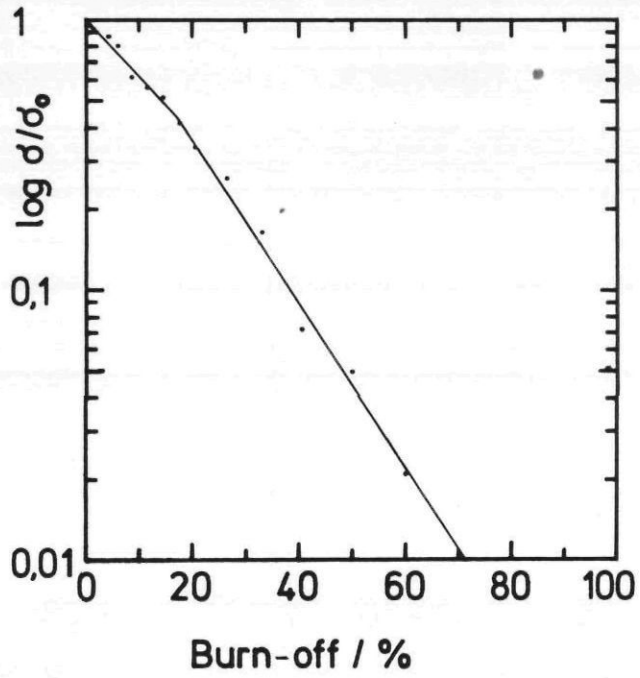

Fig. 3: Plot of relative compression strength vs. burn-off (coke filler material)

KERNFORSCHUNGSANLAGE JÜLICH GMBH

Manufacturing and Application of Coat-Mix Materials

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2) Kernforschungsanlage Jülich GmbH, D-5170 Jülich 1, P.B. 1913
3) Caron Formtechnik, D-5810 Witten 3, Rauhe Egge 21

SUMMARY

A moulding material developed for nuclear purposes based on carbon fillers and phenolformaldehyde resin binders, the so-called coat-mix material, has gained significance also for the glass industry and foundries. One of its advantages is e.g. the high fidelity of surface reproduction of a model. The process of manufacture, properties of the material, examples for applications, and further developments will be presented.

MANUFACTURING

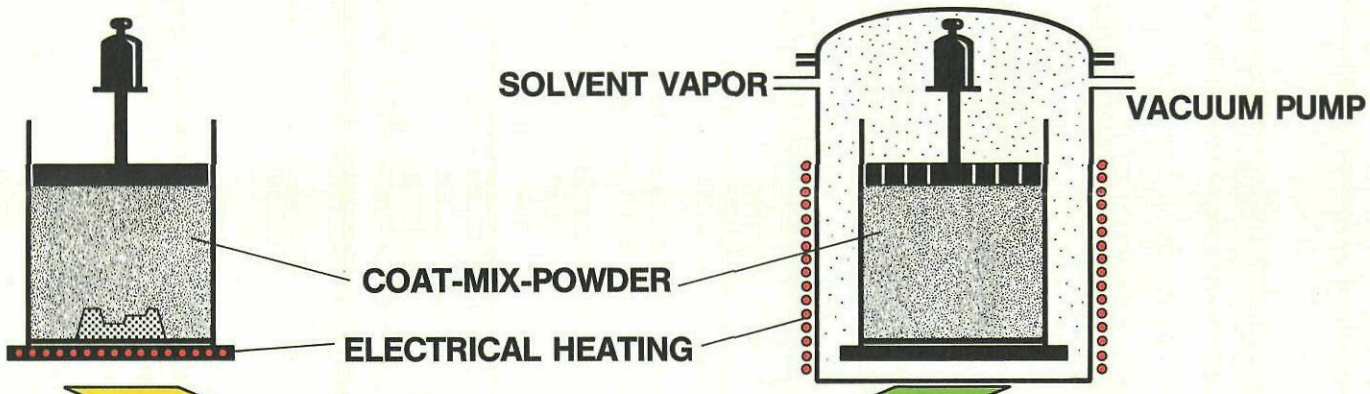
MIXING

FILLER GRAINS

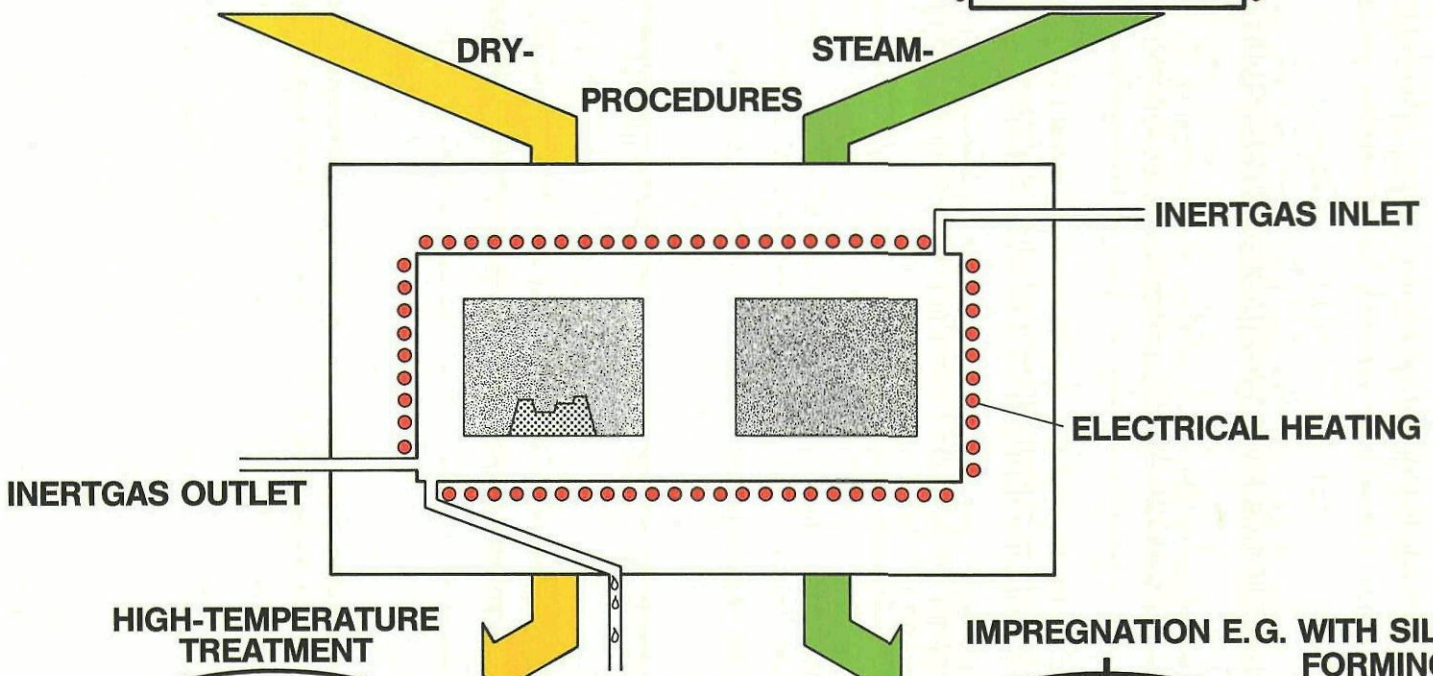
COAT-MIX-PROCEDURE

BINDER COATED FILLER GRAINS

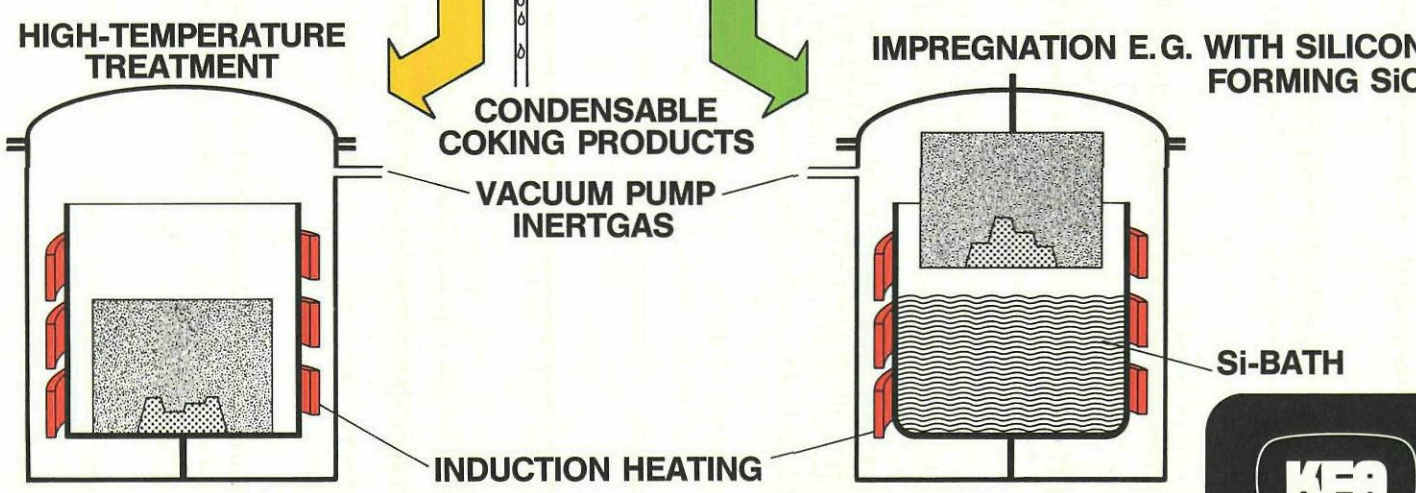
MOULDING



COKING



HIGH-TEMPERATURE TREATMENT OR IMPREGNATION



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PHYSICAL PROPERTIES

		Filler	
		Graphite	Petroleum coke
density	(g/cm^3)	0,95-1,20	0,70-1,30
porosity, total	(%)	45-65	40-70
porosity, open	(%)	35-60	30-60
gas permeability	(cm^2/cm cw min)	1,0-4,0	1,0-2,5
bending strength	(N/mm^2)		
perpendicular to grain orientation		9,5-20	12-17
crushing strength	(N/mm^2)		
perpendicular		17-35	50-80
parallel to grain orientation		17-32	50-70
modulus of elasticity	(kN/mm^2)		
perpendicular		4-8	7,0
parallel to grain orientation			5,0
CTE	($K^{-1} \times 10^{-6}$)		
perpendicular		2,10-2,85	3,80-4,40
parallel to grain orientation			5,30-5,90
specific electrical resistance	(mm^2/m)	28,0-47,0	65,0-90,0
thermal conductivity	(W/K cm)	0,1-0,17	0,03

FEATURES FOR INDUSTRIAL APPLICATIONS

- **homogeneity and isotropy of the material**
- **continuous porosity up to about 50 %**
- **high resistance due to temperature and thermal shock**
- **easy moldable for the production of prints**
- **good machinability using conventional machines and tools**
- **wide scope of possible variation of the properties for technical and economical demands.**

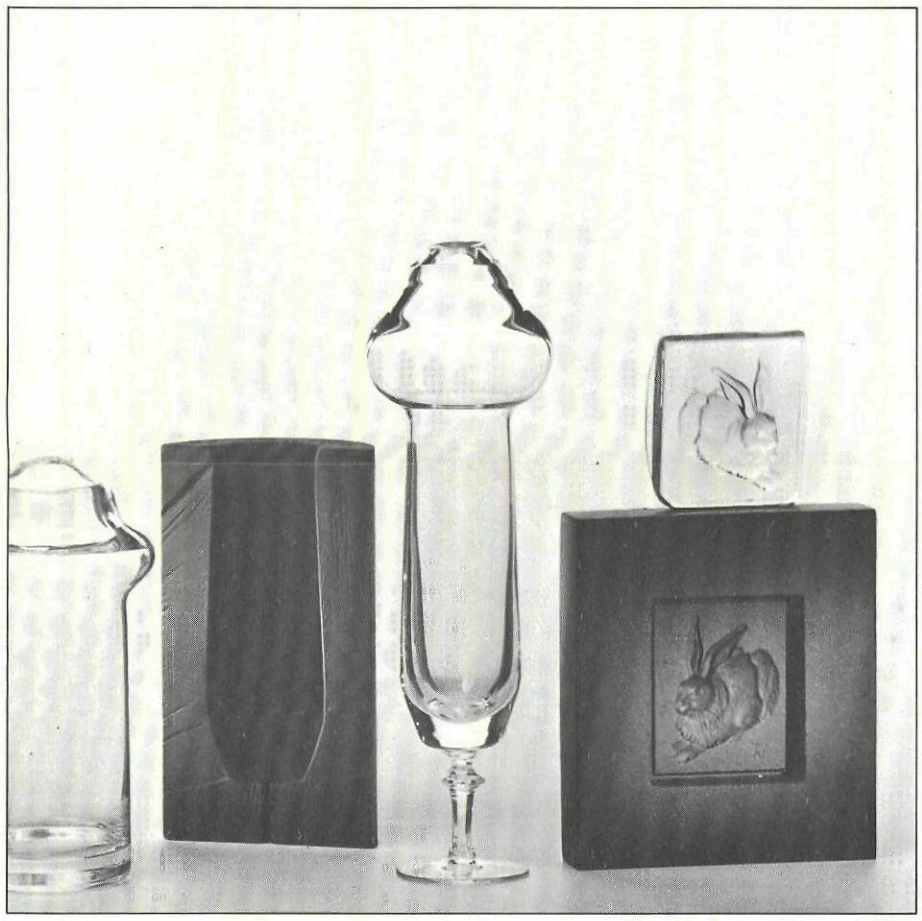

Fig.1

Fig.2

GLASSINDUSTRIES

In glass production a coat-mix mould assures high quality glass surfaces without altering the known production techniques. Fig. 1 shows two examples of manufactured lead glasses and a reproduction of a Dürer motive with cast glass, showing even smallest details of the mould negative reproduced in the glass positive. In this case the mould was obtained by direct copying of a positive gypsum model with plastified coat-mix powder material.

METALLINDUSTRIES

Experiments so far show that the material is a good moulding material for foundry work rendering high quality surfaces as well as good crystalline structures. The risk of gas inclusions in the cast body is extremly reduced due to the good gas transparency of the material. Fig. 2 shows an example of a cast medal (tin) giving an impression of the high surface quality and high accuracy in the reproduction of smallest details of the mould.

COAT-MIX BASED SILICON CARBIDE

Based on the carbon coat-mix technology a SiC material is at present in its final development stage. The essential features of this material are the same as of the carbon coat-mix material as there are homogeneity, isotropy, continuous porosity. In addition to these characteristics this material offers the well known advantages of SiC like high corrosion resistance at high temperatures and hardness. Of essential importance with respect to other known SiC materials is the fact that the coat-mix material can be treated mechanically after the coking process prior to the SiC formation in a high temperature process with the same ease as the carbon materials. The final shape and dimensions of such a machined component are not altered during the high temperature treatment. Thus the material offers completely new possibilities for an economic production of SiC components in particular of those having complicated shapes.

MANUFACTURING STEPS

Coating of C and Si particles corresponding to the coat-mix process → Moulding → Coking of the binder (T: 800° C) → Machining if nessecary → Heat treatment (T: 1800° C): formation of SiC

Some possible fields of industrial application are:
- **moulding material for metals foundry work**
- **manufacturing material for ceramic components**
- **grinding material**
- **high temperature filters.**

KFA

Optimized Graphitic Matrix Materials for Spherical HTR Fuel Elements

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OBJECTIVE:

Development and irradiation testing of graphitic matrix materials suitable for use as structural materials for HTR fuel elements

MATERIAL DEVELOPMENT:

NUKEM/HOBEG, Hanau, Fed. Rep. Germany

IRRADIATIONS:

Joint irradiation programme with the partners:
OECD-DRAGON Project, Dorchester, England
Kernforschungsanlage Jülich GmbH, Fed. Rep. Germany
EURATOM, Brussels, Belgium
Stichting Energieonderzoek Centrum Petten, The Netherlands

TEST REACTOR:

High Flux Reactor Petten, The Netherlands

RESULTS:

- Availability of 2 optimized structural materials suitable for the fuel elements of the AVR and THTR reactors:

  Standard matrix A3-3

  – successfully proved in AVR reactor operation
  – used for THTR fuel elements

  Matrix with synthesized resin A3-27

  – being tested in AVR reactor operation

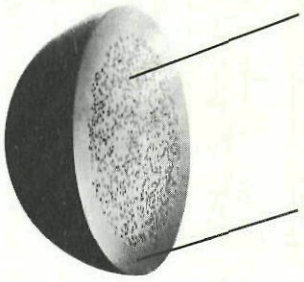
- Determination of 3 further structural materials as a potential for technological use:

  Standard matrix variants A3-6, A3-5, A5-2

- Determination of influences by
  – raw material parameters
  – fabrication parameters
  – irradiation parameters

  on material properties and their changes under irradiation which enables good understanding of the material behaviour

APPLICATION IN SPHERICAL HTR FUEL ELEMENTS



Fuelled zone:
Graphitic matrix used as a homogeneous envelopment of the coated fuel particles

Fuel-free zone:
Graphitic matrix used as a shell of the fuel element

MATERIAL DEVELOPMENT

PHASE I

Raw Materials:	Natural graphite Petroleum coke graphite Phenolic resin binder
Fabrication:	Preparation of the raw material mixture Quasi-isostatic cold moulding Heat treatment up to 1800 or 1950°C

▼

Standard matrix A3-3

▼

PHASE II
Modifications of the standard matrix

Targets of development		
1. Enlargement of raw material base	2. Simplification of fabrication	3. Improvements of product properties
Parameters varied		
○ Type of natural graphite ● Type of artificial graphite ● Degree of graphitization of the petroleum coke graphite	● Heat treatment temperature ● Synthesis of resin binder and binder type	○ Filler composition ● Binder content ○ Binder type ○ Grain size of natural graphite
▼	▼	▼ ▼
A3-6	**Matrix with synthesized resin A3-27**	**A3-5** **A5-2**

STANDARD MATRIX A3-3 AND ITS MOST FAVOURABLE VARIANTS

Designation of variant	Falling strength Fall of a test sphere from a height of 4 m onto a bed of A3-3 spheres (Number of falls till fracture) 0 200 400 600 800	Corrosion rate 10 h at 1000°C in He of 1 bar with 1 vol. % H_2O ($mg \cdot cm^{-2} h^{-1}$) 0 0.5 1.0 1.5	Irradiation behaviour Dimensional change at THTR operation time dose	Irradiation behaviour Volume shrinkage at 1250°C and THTR operation time dose
A3-3			isotropic	6 vol %
A3-27			anisotropic for T > 1000°C	slightly greater than A3-3
A3-6			mainly isotropic	slightly smaller than A3-3
A3-5			anisotropic for T > 800°C	smaller than A3-3
A5-2	> 5000	not determined	anisotropic for T > 700°C	corresponding to A3-3

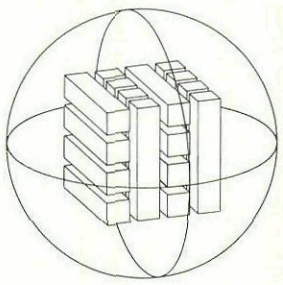
IRRADIATION TESTING

Irradiation Experiments for Testing Graphitic Matrix Materials

- Irradiation experiments
  - Isothermal test series in the HFR Petten
  - Creep experiments in the HFR Petten and in the DRAGON Reactor
- Measurements
  - out of pile between the irradiation intervals
  - Determination of the changes of dimensions and physical properties
  - Determination of creep data
- Irradiation specimens
  - for measurements of basic data

    cut out of fuel-free matrix spheres parallel and perpendicular to the equatorial plane
  - for measurements of creep data

    dumb-bell shaped specimens cut out of fuel-free matrix spheres

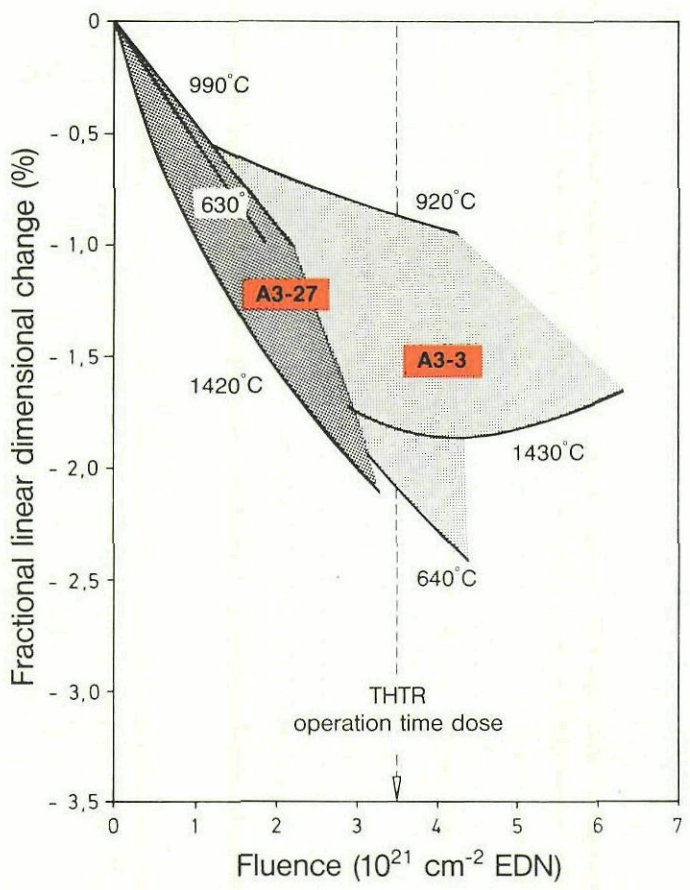


Investigated Behaviour of Graphitic Matrix Materials under Fast Neutron Exposure

- Linear dimensional change
- Young's modulus of elasticity
- Thermal conductivity
- Specific electrical resistance
- Apparent density
- Coefficient of linear thermal expansion (for A3-3)
- Creep coefficient (for A3-3)

TWO IMPORTANT IRRADIATION RESULTS

Irradiation-Induced Dimensional Changes of the Fuel Matrices A3-3 and A3-27



Irradiation-Induced Dimensional Changes of the Standard Matrix A3-3 and of Spherical Fuel Elements